

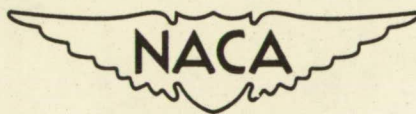
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 1915

ELEVATED-TEMPERATURE PROPERTIES OF SEVERAL
TITANIUM CARBIDE BASE CERAMALS

By George C. Deutsch, Andrew J. Repko
and William G. Lidman

Lewis Flight Propulsion Laboratory
Cleveland, Ohio



Washington
July 1949

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 1915

ELEVATED-TEMPERATURE PROPERTIES OF SEVERAL

TITANIUM CARBIDE BASE CERAMALS

By George C. Deutsch, Andrew J. Repko
and William G. Lidman

SUMMARY

An investigation was made to determine the properties of ceramals of titanium carbide plus refractory metals and to study the fundamental nature of ceramals. The properties evaluated were elevated-temperature tensile strength, elevated-temperature modulus of rupture, coefficient of linear expansion, and density. A study was also made of the microstructure of the ceramals and of the coatings formed during exposure to oxidizing conditions.

This investigation yielded the following results:

1. The ceramals exhibiting the highest strengths as determined by modulus-of-rupture tests were:

(a) Titanium carbide (80 percent) plus cobalt (20 percent) at 1600° F, 57,800 to 100,800 pounds per square inch.

(b) Titanium carbide (80 percent) plus cobalt (20 percent) at 2000° F, 29,400 to 71,900 pounds per square inch.

(c) Titanium carbide (90 percent) plus molybdenum (10 percent) at 2400° F, 16,100 to 20,900 pounds per square inch.

2. The densities of the ceramals studied were from 0.4 to 11.2 percent of those of mechanical mixtures of the original constituents.

3. The oxidation characteristics of the ceramals investigated were affected considerably by the oxidation characteristics of the metal constituent.

4. The strengths of the ceramals investigated might be due to the presence of a chemical combination of the two original constituents.

5. On the basis of the bonding theory presented, it is probable that the strengths of ceramals varied with particle size.

6. For the given fabrication technique and ceramic-particle size, an optimum percentage of metal constituent for best properties existed.

7. The use of metals having better refractory properties imparted higher strengths at the higher evaluation temperatures.

As a result of the investigation, titanium carbide base ceramals are considered promising as gas-turbine-blade materials in the temperature range of 1600° to 2400° F.

INTRODUCTION

The specific fuel consumption of turbine-type aircraft-propulsion systems can be improved if permissible operating temperatures are increased. Existing data indicate little possibility of obtaining satisfactory service lives from existing alloys at turbine-blade operating temperatures significantly higher than those currently used. One phase of the research to provide materials that will withstand more severe operating conditions is the investigation of materials consisting of combinations of metals and ceramics. Certain combinations of such composite materials, ceramals (references 1 and 2), are considered to combine the desirable high-temperature strength property of ceramics with the high resistance to mechanical and thermal shock of metals.

Early work with tungsten carbide - cobalt combinations (reference 3) on the nature of the ceramic-metal bond led to the hypothesis that at low metal contents the metal additions act principally as catalysts to aid in the formation of a strong ceramic skeleton. At higher metal contents, the added metal tends to envelop the ceramic particles and bond them together in a continuous metal network.

An investigation intended as a preliminary study to determine the properties of ceramals containing titanium carbide plus refractory metals and to study the fundamental nature of ceramals was conducted at the NACA Lewis laboratory.

Titanium carbide was chosen as the ceramic constituent for its thermal-shock characteristics and relatively high elevated-temperature strength (reference 4). Cobalt was chosen as a bonding element because experience in the tool industry has long indicated the efficiency of cobalt as a bonding element for carbides. Molybdenum and tungsten were also used as bonding elements to determine the effects of additions of other refractory metals on the high-temperature properties of ceramals. All ceramals were evaluated with 5, 10, 20, and 30 percent by weight of metal content.

The properties evaluated were elevated-temperature tensile strength, elevated-temperature transverse-bending strength, density, coefficient of linear expansion, and oxide-coating composition and structure.

Densities of all bodies evaluated were determined in order to compare ceramals with ceramic and alloy bodies on the basis of strength-to-weight ratios and in order to obtain information on the bonding mechanism (reference 5).

Linear-expansion coefficients were measured to permit determination of tip clearances for ceramal turbine blades and to permit calculation of the resistance to thermal shock.

The oxide coatings developed on the specimens during evaluation were studied to determine their composition so that in the event a ceramal has desirable strength properties suitable additions, based on past experience in the ceramics industry, could be made to make the coating both impervious and tightly adhering.

The microstructure of the bodies was studied to obtain information about the bonding mechanisms that were responsible for the elevated-temperature characteristics.

No time-dependent properties such as stress-rupture strength and creep rate were determined because of a lack of available facilities.

APPARATUS AND PROCEDURE

All bodies used in this investigation were fabricated by Kennametal, Inc. according to the following procedure. The 325 mesh and fines ceramic and hydrogen-reduced metal constituents were ball-milled together in steel mills using tungsten carbide balls in a chemically inert organic liquid carrier. Tungsten carbide contamination in milling resulted in approximately two-thirds of 1 percent tungsten carbide in the ceramals containing cobalt and $5\frac{3}{4}$ percent in the ceramals containing molybdenum and tungsten. Wax was incorporated into the blended and milled powders for green strength. Compacting was performed cold using pressures from 50,000 to 60,000 pounds per square inch. Bodies were preformed in the semisintered state and the final sintering was accomplished by induction heating in vacuum at the following temperatures:

Titanium carbide (TiC) plus cobalt (Co) compositions, °F	2800 - 3200
Titanium carbide (TiC) plus tungsten (W) compositions, °F	3500 - 3800
Titanium carbide (TiC) plus molybdenum (Mo) compositions, °F . . .	3100 - 3800

Bodies were finish-ground using diamond abrasives after sintering.

Tensile-strength evaluation. - Elevated-temperature tensile evaluations were conducted at 1800° and 2200° F using the NACA specimen for brittle materials (fig. 1) and the procedure described in reference 6.

The apparatus used consisted of a hydraulic tensile machine (fig. 2) equipped with a load-maintaining device and a device that permitted constant rate of load application. The specimen was held in high-temperature-alloy grips inside a furnace. The 1800° and 2200° F evaluations were conducted using a platinum-wound electric furnace and control thermocouples of platinum - platinum-rhodium.

The bending stresses in the specimen were measured at room temperature and with a load of 400 pounds by four wire strain gages mounted 90° apart on the test section. The specimen was adjusted to minimize the bending stresses.

The specimens were subjected to a soaking period at 100° F above the evaluation temperature with a nominal load on the specimen of 100 ±15 pounds and with a constantly flowing helium atmosphere. The rate of load application during the evaluation was 400 pounds per minute.

In those cases in which the helium atmosphere did not afford complete protection and the specimens were oxidized, the diameter after test and exclusive of scale was used to compute the tensile strength. Because the length of time of the soak was much longer than the evaluation time, the assumption was made that practically all the oxidation occurred in the soaking period and consequently a specimen of reduced diameter was evaluated. The maximum reduction in area as the result of oxidation of the specimen was 12.5 percent. During the course of the investigation, the length of the soak was found to be a minor variable. The soaking period was therefore reduced from overnight to 4 hours.

Specimens were inspected upon receipt for dimensional conformity to specifications and for internal and external flaws by radiographic and fluorescent-oil methods, respectively.

Modulus-of-rupture evaluation. - The modulus of rupture of ceramals was evaluated at 1600°, 2000°, and 2400° F to cover the estimated range of utility. The elevated-temperature short-time modulus-of-rupture apparatus (fig. 3) consisted essentially of a commercial nonmetallic-resistor furnace into which the required lever system and the chamber for the helium protective atmosphere were incorporated. The specimen was placed on two silicon carbide knife edges, which were cemented $3\frac{3}{4}$ inches apart on a refractory brick. Loading was accomplished by a lever

system that caused the third (upper) knife edge, also of silicon carbide, to press down on the specimen midway between the two supporting knife edges. All knife edges were rounded to 1/8-inch radius to minimize stress concentrations at the contact points. Loading was accomplished at the same rate as used in tensile evaluation (2000 (lb/sq in)/min) by running water into a container supported on the lever arm of the upper knife edge. Care was exercised to run the water down the side of the container to avoid any impact loading effects. The lever-arm ratio of the loading arm was 9.

The specimens used in the evaluation were nominally 1/4 inch thick, 1/2 inch wide, and 4 inches long. They had diamond-ground surfaces and were inspected in the same manner as the tensile-evaluation specimens. Soaking the specimens overnight at a temperature 100° F above the evaluation temperature was originally planned. Initial evaluations indicated, however, that the length of the soak was a minor variable; consequently, in order to avoid the risk of excessive oxidation and to speed up results, the soaking period was eliminated on the 2400° F evaluations and reduced to 4 hours after equilibrium was attained on the 1600° and 2000° F evaluations.

As a specimen fractured, the loading arm fell and actuated a solenoid valve that shut off the flow of loading water. The weight of water plus container was determined with a balance accurate to 1/8 pound. Trial runs indicated that not more than 2 ounces of water would run into the container in the time required for the solenoid valve to shut off completely the water flow. If both of these errors were additive, the total error introduced in the modulus-of-rupture value would be 400 pounds per square inch. After fracture, the specimens were immediately removed from the furnace and water-quenched to prevent oxidation.

For the 1600° and 2000° F evaluations, helium was used as the protective atmosphere with a flow rate of 40 cubic feet per hour. At the evaluation temperature of 2400° F, argon was used with a flow rate of 50 cubic feet per hour. The change from helium to argon was necessitated by the difficulty of retaining helium at the higher temperature in a chamber that could not be tightly sealed. Evaluation temperatures were controlled by shielded thermocouples placed adjacent to the specimen. For the 1600° and 2000° F evaluations, chromel-alumel thermocouples were used, whereas platinum - platinum-rhodium thermocouples were used at 2400° F. Any deflection of the specimens was measured by a pointer attached to the loading-lever arm. With this arrangement, deflections of 0.01 inch could be detected.

In those cases in which the protective atmospheres did not afford complete protection and the specimens were oxidized, the dimensions after evaluation were used to compute the modulus-of-rupture strength. This procedure is justifiable for the 1600° and 2000° F evaluations because the assumption can be made that practically all the oxidation occurred in the lengthy soaking period and the specimen evaluated was of reduced size. Practically no oxidation occurred at 2400° F because of the short soaking period.

The modulus-of-rupture strength was calculated from the equation

$$S = \frac{3}{2} \left(\frac{pd}{wt^2} \right)$$

where

- S modulus-of-rupture strength, pounds per square inch
 p load on specimen (measured load times lever ratio), pounds
 d distance between supporting knife edges, inches
 w specimen width, inches
 t specimen thickness, inches

Density determinations. - The densities of all bodies evaluated were determined by dividing the weight of the body in air by the loss in weight when the body was weighed in water. All weighings were performed on an analytical balance. The individual values reported are believed to be correct to within ± 0.01 gram per milliliter.

The calculated densities were determined using the following equations:

$$a_c + a_m + \left(\frac{b_w w}{100} \right) \left(\frac{195.95}{183.94} \right) = W$$

where

- a_c nominal percentage by weight of ceramic
 a_m nominal percentage by weight of metal
 b_w percentage by weight of tungsten in tungsten carbide contaminant as determined by chemical analysis (For ceramals containing tungsten, this value was assumed to be the same as that for ceramals containing molybdenum.)

W total weight of ceramal including tungsten carbide contaminant,
grams

195.95 molecular weight of tungsten carbide

183.94 molecular weight of tungsten

and

$$\frac{a_c}{W\rho_c} + \frac{a_m}{W\rho_m} + \left(\frac{b_W}{\rho_{WC}100} \right) \left(\frac{195.95}{183.94} \right) = \frac{1}{\rho_b}$$

where

ρ_b density of ceramal body, grams per milliliter

ρ_c density of ceramic constituent, grams per milliliter

ρ_m density of metal constituent, grams per milliliter

ρ_{WC} density of tungsten carbide contaminant, grams per milliliter

These equations are based on the supposition that a mechanical mixture of the ingredients exists.

Oxide-coating studies. - The oxide films formed on the bodies during evaluation were studied by X-ray diffraction methods. In those cases in which no film was developed during evaluation, the specimens were oxidized in a small muffle furnace without a protective atmosphere at 2400° F. Oxide, scraped from representative specimens, was finely ground and X-ray diffraction patterns were made using Debye-Scherrer cameras 114.6 and 143.2 millimeters in diameter. Filtered cobalt K-alpha and copper K-alpha radiations were used. Identification of components was made by comparing the patterns obtained with those tabulated in the A.S.T.M. X-ray diffraction-card index.

Coefficient-of-linear-expansion determinations. - A commercial interferometer was used to determine the coefficient of linear expansion from room temperature to 1112° F of each composition evaluated. The specimens needed for each determination were three right pentahedral pyramids. Above 1112° F the specimens reacted chemically with the fused quartz optical flats of the apparatus and introduced errors into the reading even though an inert argon atmosphere was provided. Consequently, values only to 1112° F are reported.

The calculated coefficient of linear expansion was determined using the following method:

$$\alpha_b = \frac{\alpha_c \frac{W_c}{\rho_c} + \alpha_m \frac{W_m}{\rho_m} + \alpha_{WC} \frac{W_{WC}}{\rho_{WC}}}{\frac{W_c}{\rho_c} + \frac{W_m}{\rho_m} + \frac{W_{WC}}{\rho_{WC}}}$$

where

W_c weight of ceramic, grams

W_m weight of metal, grams

W_{WC} weight of tungsten carbide contaminant, grams

α_b linear coefficient of ceramal body, inches per inch per $^{\circ}\text{F}$

α_c linear coefficient of ceramic, inches per inch per $^{\circ}\text{F}$

α_m linear coefficient of metal, inches per inch per $^{\circ}\text{F}$

α_{WC} linear coefficient of tungsten carbide contaminant, inches per inch per $^{\circ}\text{F}$

Here again the assumption was made that a mechanical mixture of the constituents exists.

Structure studies. - Studies of the structures of each composition evaluated were made using standard metallographic methods with reflected light. Preparation of the specimens was accomplished using standard metallographic wheels with diamond abrasives.

Chemical analyses. - Chemical analyses were obtained for representative specimens of each composition evaluated so that errors in compounding or marking of the specimens as well as the presence of impurities could be detected. These wet analyses were performed by two commercial laboratories and by the fabricator.

BONDING THEORY

The function of added metal to ceramics is principally to impart better resistance to fracture by thermal shock. The choice of the added

metal should be such as to retain or to improve the physical strength of the ceramic. The function of the added metal may be achieved by the mechanism described in reference 3 or by bonding the ceramic particles together while separating them with a thermal-shock-resistant layer. In order for the ceramic particles to be held together, a chemical or mechanical bond must exist.

Mechanical bonding can be achieved by (1) interlocking the ceramic particles with the metal particles or by (2) interlocking of the ceramic particles with other ceramic particles with the metal filling the voids formed by the interlock. In the first case, the strength of the body would be that of the weaker constituent and is undesirable because the elevated-temperature strength is limited by the softening point of the lower melting constituent; the second case is also thought to be undesirable because the thermal-shock characteristics of the body would be nearly those of the original ceramic material inasmuch as the ductility modulus would be nearly that of the ceramic constituent.

A chemical bond may exist as either a solid solution or a compound of the original ingredients. The possibility exists that a chemical compound of the constituents would be stronger than either constituent, thus improving the strength of the composite body as well as enveloping it in a shock-resistant network. Theoretically, a solid solution would be better because the possibility of anticipating the properties of the new phase is greater.

The required minimum quantity of chemically formed bonding material is the amount necessary to envelop each ceramic particle completely, thus forming a continuous network. For a fixed thickness of bonding material around the particles and for a given volume of particles, the amount of bonding material required for complete enveloping increases with decreasing ceramic-particle size.

In the case where the ceramic particles approximate spheres, the ratio of area to volume is equal to

$$\frac{A}{V} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R}$$

where

A surface area of particle, square inches

V volume of particle, cubic inches

R radius of particle, inches

Assuming the mass volume to be constant reduces the equation to

$$A = \frac{K}{R}$$

where

K constant of proportionality

Thus the total area is inversely proportional to the particle radius. Consequently, for a given volume of ceramic particles, for example, a 50-percent reduction in average particle radius, the increase in surface area is doubled and the amount of metal required to form the bonding material necessary for complete enveloping is increased in the same proportion. If a constant ceramic-particle size were used, the strength of each combination would be expected to show a peak with respect to the percentage of metal because below this peak value insufficient metal would be present to form the amount of bonding material required and above this peak value excess metal would be present.

The peak strength value can further be expected to vary inversely with the ceramic-particle size and to vary directly with the metal content because greater bonding efficiency is achieved with smaller particle size.

A solid-solution bonding material can be expected to be more refractory if constituents with better refractory properties are used.

From the previously mentioned consideration, the following criterions by which chemical bonds can be recongnized may be established: The microstructure shows a rounding of the grains and the percentage of each constituent in the microstructure is different from that expected from the composition of the body. If a chemical bond is present, the density of the body is expected to be different from that calculated on a mixture basis of the original constituents. If the strength of a ceramal body exceeds the strength calculated on a volume basis from the strength of the initial constituents, chemical bonding exists.

RESULTS

Elevated-temperature strength evaluations. - The inspection results of all specimens used for tensile-strength and modulus-of-

rupture evaluations are given in tables I and II, respectively. Table III presents the results obtained in the short-time tensile-strength evaluation, and tables IV to VI the modulus-of-rupture evaluation. Variations of tensile strength with compositions for titanium carbide plus cobalt are shown in figure 4 at two evaluation temperatures. The trends in modulus-of-rupture strength at evaluation temperatures with composition for all the ceramals evaluated are shown in figure 5. For these curves, only the peak values experimentally obtained were used. These peak values can be assumed as most nearly representing the maximum potentialities of each composition. For a preliminary evaluation of this type, these values are of greatest interest. All further discussion of strengths is on the basis of the peak values.

At 1800° F, the best ceramal composition (20-percent cobalt and 80-percent titanium carbide) evaluated has a tensile strength of 34,600 pounds per square inch (table III). At the same evaluation temperature, the basic ceramic material, titanium carbide, has a tensile strength of 15,850 pounds per square inch (reference 4).

Because neither necking in the tensile evaluation nor deflection in the modulus-of-rupture evaluation was noted, none of the bodies can be considered plastic. Data obtained at the Engineering Experiment Station, Ohio State University, indicate that the modulus-of-rupture strength for brittle materials is generally from 1.67 to 2.5 times the tensile strength. By assuming that these values apply and by interpolating the modulus of rupture of the ceramals containing cobalt to 1800° F, a modulus-of-rupture strength from 2.2 to 2.5 times the tensile strength for the 5-, 10-, and 20-percent-cobalt ceramals results. However, the ratio for the 30-percent-cobalt ceramal is 3.6. This discrepancy probably indicates that the reported tensile strengths for the 30-percent-cobalt ceramal at 1800° F are somewhat low.

A comparison of the strength-to-weight ratios of the best titanium carbide plus cobalt, molybdenum, or tungsten ceramals with a typical high-temperature alloy at 1800° F is presented in table VII. This comparison could not be made at 2400° F because most high-temperature alloys are between their solidus and liquidus temperatures. At 1800° F, all ceramals show higher strength-to-weight ratios than the high-temperature alloy, and the ceramal containing cobalt, which is the best at this temperature, exceeds the alloy by 60 percent. On this basis ceramals appear promising as gas-turbine-blade materials in the temperature range of 1600° to 2400° F.

Chemical analyses. - The results of the chemical analyses, made by a commercial laboratory, together with check analyses by another commercial laboratory and by the fabricator, are presented in table VIII.

Although these analyses are difficult to perform, the inaccuracies are believed not to exceed 2 percent of the values reported. The reported low bonding-metal contents of the ceramals is believed due to dilution of the powders by the tungsten carbide contaminant and to losses encountered during vacuum sintering.

Density evaluation. - The average measured density of the modulus-of-rupture specimens of each composition and a corresponding calculated value are shown in table IX and are plotted in figure 6. The permissible variation in densities of experimental bodies of this type is about 10 percent. Within this variation, satisfactory agreement exists between the calculated value based on nominal composition plus average percent contaminant and the average measured values. Variations in density measurements for each ceramal composition are believed to be the result of fabrication and composition variables; these variations justify the use of average values of density for correlation purposes. The densities in all instances are lower than the calculated values. No correlation could be found between the "apparent" or "effective" densities in the inspection radiographs (table II and fig. 7(a)) and the measured densities.

Linear-expansion studies. - The results of the studies of the coefficients of linear expansion are presented in table X and in figure 8. The results shown are peak values from duplicate determinations.

For purposes of calculating clearances, these peak values may be of great interest. In all cases, the duplicate determinations resulted in values that were within 1 percent of each other. Table X also presents calculated linear-expansion coefficients for each composition. The coefficients are based on the assumption that a mechanical mixture of nominal composition with average tungsten carbide contamination exists, as reported in the chemical analysis for each type ceramal. The linear coefficients of expansion of each constituent that was used for these calculations are:

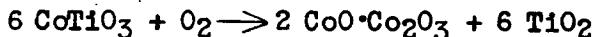
Titanium carbide, (in./in.)/ $^{\circ}\text{F}$	4.12×10^{-6}
Tungsten carbide, (in./in.)/ $^{\circ}\text{F}$	2.6×10^{-6}
Cobalt, (in./in.)/ $^{\circ}\text{F}$	10.05×10^{-6}
Tungsten, (in./in.)/ $^{\circ}\text{F}$	2.5×10^{-6}
Molybdenum, (in./in.)/ $^{\circ}\text{F}$	3.1×10^{-6}

(The value for tungsten carbide is from reference 3 and other values are data from various standard handbooks.)

As expected, the ceramals containing cobalt exhibit the highest coefficients. In ceramals containing tungsten or molybdenum, the coefficients decrease with increasing metal content whereas in ceramals containing cobalt, the coefficients increase with increasing metal content. This difference again is the expected result because tungsten and molybdenum have lower coefficients than does the principal ceramic constituent, titanium carbide, whereas cobalt has a higher coefficient.

Oxide-coating investigation. - All X-ray diffraction patterns of the coatings developed on the specimens showed strong lines of titanium dioxide TiO_2 . In addition to titanium dioxide, those ceramals containing tungsten all showed the presence of tungsten trioxide WO_3 , whereas those containing 20 to 30 percent of molybdenum were found to contain molybdenum trioxide MoO_3 . The reason for the absence of molybdenum trioxide in the ceramals containing 5 to 10 percent of molybdenum is unknown; however, molybdenum trioxide is extremely volatile and probably volatilized from the surface as fast as it was formed. The X-ray diffraction patterns of the oxide coatings of ceramals containing either molybdenum or tungsten, evaluated at the highest temperature, had lines superimposed on the pattern that are believed to be lines of the metal constituent. Positive identification of the metal constituent in the oxide coating was impossible because there were too few lines. Ions of the bonding element are believed to migrate through the oxide layer and combine with oxygen at the oxide-atmosphere interface.

The ceramals containing cobalt developed a two-layer oxide. The inner layer consisted of cobalt titanate $CoTiO_3$ plus some faint lines of titanium dioxide. The outer layer consisted of a higher proportion of titanium dioxide plus a spinel having a lattice parameter of 8.10 angstrom units. This spinel is believed to be cobaltous cobaltic oxide $CoO \cdot Co_2O_3$. The outermost layer is probably the result of further oxidation of the initially formed inner layer. This oxidation could occur during a reaction such as



The oxidation characteristics of these ceramals are discussed in greater detail in reference 7, which shows that the resistance to oxidation of all ceramals studied decreases with increasing metal content. Inasmuch as the oxides of the metallic constituents were found in the oxide layers formed on the ceramals during the evaluations, the oxidation characteristics of these ceramals are altered by the various added metals.

DISCUSSION OF RESULTS

On the basis of the data presented in this investigation and the data presented in reference 3, it is impossible to conclude which theory of bonding most nearly describes the mechanism existing in ceramals. The bonding mechanism that exists is probably a combination of the two mechanisms described and may change with different combinations of ceramics and metals. Different mechanisms have been observed with varied percentages within one ceramic-metal combination. For high-temperature and high-shock applications, the development of the bonding layer in ceramals appears to be more desirable.

Microstructure study. - A study of the microstructures of titanium carbide ceramals containing cobalt, tungsten, or molybdenum (figs. 9, 10, and 11, respectively) showed rounding of the ceramic particles, which is an indication that chemical action has occurred. Neither the cobalt nor the molybdenum ceramals (figs. 9 and 11) showed the 19.5- and 17.2-percent metal content, respectively, that would be expected on a volume basis; this difference is indicative of chemical action. Figure 10 shows the presence of the approximate amount of tungsten (10 percent) that would be expected on a volume basis if a solid solution existed; this amount indicates that the limit of solubility is low. From these figures it also appears that little or no mechanical interlocking of the particles occurs.

Density evaluation. - Densities can indicate the type of bond that exists in the ceramal. First, the lattice parameter of the ceramic constituent, titanium carbide, was measured by back-reflection X-ray diffraction methods and was found to be 4.31 angstrom units. With this value and the crystal structure (reference 8) known, the density of the titanium carbide was calculated as 4.96 grams per milliliter, which is also confirmed in reference 8. The calculated value is different from the value of 4.25 grams per milliliter published in most handbooks. Use of this value and the assumption that a mechanical mixture of the constituents exists give a calculated value of the density that is within approximately 10 percent of the measured value and, as expected, increases with increasing metal content (fig. 6).

In the case of ceramals containing cobalt, a combination with which the fabricator has had considerable experience, the agreement between the calculated and measured values of density is within 4 percent. However, if the assumption were made that all the cobalt went into a substitutional solid solution into the lattice of the titanium carbide and thereby replaced the titanium atoms and left the lattice deficient in carbon, the calculated density (4.5 to 4.8 grams/ml depending on certain assumptions concerning the lattice parameter for the ceramal of 80-percent titanium carbide plus 20-percent cobalt) is

much lower than the measured value. Because of the differences in atomic sizes, the assumption that the cobalt atoms would replace carbon atoms in a substitutional solid solution would be illogical. The converse assumption that the titanium carbide might go into solution in the lattice of cobalt is illogical because the generated volume is not evident from the photomicrographs. But, it can be assumed that the cobalt goes into an interstitial solid solution in the titanium carbide lattice, even though the probability is low. Calculations based on this assumption (for example, the ceramal of 80-percent titanium carbide plus 20-percent cobalt has a density of 6.2 grams/ml) yield a much higher density than measured values. These calculations show that most of the cobalt is probably still in the metal state, and the bonding material is present only in small quantities.

The greater differences between the calculated and average measured densities for the ceramals containing molybdenum or tungsten cannot be explained, but are believed to be the result of porosities present in the ceramal bodies.

Coefficient-of-linear-expansion determination. - The agreement between calculated and measured values for the coefficient of linear expansion is good. This agreement, as in the case of the density, tends to indicate that most of the original constituents are still present in the sintered body and the bonding phase is present in only small amounts. The reason why better agreement between calculated and measured values was achieved for the coefficients of linear expansion than was achieved for the densities is not yet understood. Because of bridging-over porosities, this property appears insensitive to variations in fabrication techniques, to minor fluctuations in composition, and to the presence of impurities.

Elevated-temperature strength evaluation. - In both the tensile and modulus-of-rupture evaluations of titanium carbide - cobalt ceramals, a definite peak can be noted at 20-percent cobalt up to 2000° F (figs. 4 and 5). Above this temperature, these ceramals appear to have lost practically all their strength. The titanium carbide - tungsten and titanium carbide - molybdenum ceramals also show the peaks predicted in the theory of bonding at each modulus-of-rupture evaluation temperature (fig. 5). In the ceramals containing tungsten, the peaks occur at low metal percentages, which again tends to confirm the presumed low solubility of tungsten in titanium carbide. In the ceramals containing molybdenum, two peaks in modulus-of-rupture strength are evident at the 1600° and 2000° F evaluation temperatures (fig. 5). The reason for these peaks is

unknown; however, the first peak may be due to the presence of the optimum amount of solid solution without excess metal, and the second peak may be attributed to the formation of a strengthening compound.

In addition to the fabrication and evaluation variables, discrepancies in the data (tables III to VI) may be attributed to the presence of stress concentrations. Figure 7(b) shows chemical segregation that may act as a stress raiser. If a specimen were evaluated near the top of its usable temperature range, it might have less tendency to be impaired severely by stress concentrations caused by defects than if it were evaluated at a considerably lower temperature, because on a microscopic basis the bonding material would be more plastic in the first case. As predicted in theory, the use of tungsten and molybdenum, which are more refractory than cobalt, as added metals yielded ceramals having higher strengths at the higher evaluation temperatures.

SUMMARY OF RESULTS

From investigation of the properties and fundamental nature of titanium carbide plus cobalt, molybdenum, or tungsten ceramals, the following results were obtained:

1. The ceramals exhibiting the highest strengths as determined by modulus-of-rupture tests were:

(a) Titanium carbide (80 percent) plus cobalt (20 percent) at 1600° F, 57,800 to 100,800 pounds per square inch

(b) Titanium carbide (80 percent) plus cobalt (20 percent) at 2000° F, 29,400 to 71,900 pounds per square inch

(c) Titanium carbide (90 percent) plus molybdenum (10 percent) at 2400° F, 16,100 to 20,900 pounds per square inch

2. The densities of the ceramals studied were from 0.4 to 11.2 percent of those of the mechanical mixtures of the original constituents.

3. The oxidation characteristics of the ceramals investigated were altered by the oxidation characteristics of the metal constituent.

4. The strengths of ceramals might be due to the presence of a chemical combination of the original two constituents that exist only in thin films.

5. On the basis of the bonding theory presented, it is probable that the strengths of ceramals varied with ceramic-particle size.

6. For the given fabrication technique and ceramic-particle size, an optimum percentage of metal constituent for best properties existed.

7. On a strength-to-weight ratio basis, ceramals appeared promising as gas-turbine-blade materials in the temperature range of 1600° to 2400° F.

8. The use of highly refractory metals as binder materials for ceramals appeared desirable for higher strengths at the higher evaluation temperatures.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, April 13, 1949.

REFERENCES

1. Anon.: Carbides for High Temperature Applications. Materials and Methods, vol. 26, no. 6, Dec. 1947, pp. 85-86.
2. Kopecki, E. S.: Metallurgy. The Iron Age, vol. 161, no. 1, Jan. 1, 1948, pp. 198-207.
3. Dawihl, W., and Hinnueber, J.: On the Structure of Cemented Hard Metal Compositions. Trans. No. 1545, Henry Bratcher, Co. (Altadena, Calif.), 1944. (From Kolloid Zeitschr., Bd. 104, Nrs. 2-3, 1943, S. 233-236.)
4. Gangler, James J., Robards, Chester F., and McNutt, James E.: Physical Properties at Elevated Temperature of Seven Hot-Pressed Ceramics. NACA TN 1911, 1949.
5. Hoyt, S. L.: Hard Metal Carbides and Cemented Tungsten Carbide. Trans. Am. Inst. Mining and Metallurgical Eng., Inst. Metals Div., vol. 89, 1936, pp. 9-58.
6. Hoffman, Charles A., Ault, G. Mervin, and Gangler, James J.: Initial Investigation of Carbide-Type Ceramal of 80-Percent Titanium Carbide plus 20-Percent Cobalt for Use as Gas-Turbine-Blade Material. NACA TN 1836, 1949.

7. Whitman, M. J., and Repko, A. J.: Oxidation of Titanium Carbide Base Ceramals Containing Molybdenum, Tungsten, and Cobalt. NACA TN 1914, 1949.
8. Wyckoff, Ralph W. G.: The Structure of Crystals. No. 19, Am. Chem. Soc. Monograph Ser., The Chem. Catalog Co., Inc. (New York), 2d ed., 1931, p. 228.

TABLE I - INSPECTION RESULTS OF TENSILE-EVALUATION

SPECIMENS; TITANIUM CARBIDE - COBALT CERAMALS

Specimen	Cobalt in ceramal (percent by weight)	Defect	Degree
3B			
1	5	Coarse chemical segregation	Considerable
2		None	
3		Coarse chemical segregation	Considerable
12		Coarse chemical segregation	Considerable
13		Coarse chemical segregation and porosity; surface crack in test section	Slight Small
3C			
1	10	None	
2		None	
3		None	
4		None	
11		None	
12		None	
3D			
1	20	None	
2		Fine chemical segregation	Very slight
3		Coarse chemical segregation	Slight
4		None	
5		None	
3E			
7	30	None	
8		None	
10		Coarse chemical segregation	Slight
11		Coarse chemical segregation	Slight
12		None	



TABLE II - INSPECTION RESULTS OF MODULUS-OF-RUPTURE¹

Specimen	Metal in ceramal (percent by weight)	Defect	Degree
Cobalt			
3B 5 6 7 8 9 10 15	5	Chemical segregation Chemical segregation Chemical segregation Chemical segregation Chemical segregation Chemical segregation None	Considerable Slight Slight Considerable Considerable Trace
3C 5 6 7 8 9 10	10	Chemical segregation None Chemical segregation Chemical segregation None Chemical segregation	Slight Trace Slight Trace
3D 6 7 8 9 10 11 31 32 39	20	None None None None Chemical segregation None None None Chemical segregation	 Trace Slight
3E 1 2 3 4 5 6 16 17	30	None None None None None None None None	
Tungsten			
3F 1 2 4 5 6 7 8	5	Low apparent density Low apparent density Low apparent density None None None None	Considerable but uniform Slight but uniform
3G 1 2 3 4 5 6 7 8	10	Low apparent density Coarse chemical segregation Low apparent density Coarse chemical segregation Low apparent density Coarse chemical segregation None None	Considerable Appreciable Considerable Appreciable Considerable Appreciable

EVALUATION SPECIMENS; TITANIUM CARBIDE PLUS METAL CERAMALS

Specimen	Metal in ceramal (percent by weight)	Defect	Degree
Tungsten			
3H 1 2 3 4 5 6 7	20	Low apparent density Fine chemical segregation Fine chemical segregation Fine chemical segregation Fine chemical segregation Fine chemical segregation None	Very slight Slight Slight Slight Slight Slight Slight
3I 1 2 3 4 5 6 7	30	None None None High apparent density; fine chemical segregation None None None	Slight Slight
Molybdenum			
3J 1 2 3 4 5 6 7	5	None None None None None None None	
3K 1 2 3 4 5 6 7 8	10	Low apparent density None Low apparent density None Low apparent density None None None	Very slight Very slight Very slight
3L 1 2 3 4 5 6 7	20	None None High apparent density High apparent density None None None	Very slight Very slight
3M 1 2 3 4 5 6 7 8	30	None High apparent density None None None None None	Considerable

TABLE III - TENSILE STRENGTHS OF TITANIUM CARBIDE - COBALT CERAMALS

Specimen	Metal (percent by weight)	Tensile strength (lb/sq in.)		Soak		Remarks
		1800° F	2200° F	Time (hr)	Temperature (°F)	
3B 1 3 13 2 12	5	22,600	9800	9 $\frac{1}{2}$	1900	Failed in conical end Failed in tension during soaking Failed in tension during soaking
		20,400		4	2300	
					2300	
					2300	
					2300	
3C 1 11 4 12 2 3	10	24,600	14,400 11,400	12	1900	Failed in tension during soaking Failed in tension during soaking
		18,900		4	1900	
				4	2300	
					2300	
					2300	
3D 1 5 2 4 3	20	31,800	8,900 13,200	12 $\frac{1}{2}$	1900	Failed in tension during soaking Failed in tension during soaking
		34,600		12	1900	
				13 $\frac{1}{2}$	2300	
				4	2300	
					2300	
3E 7 11 8 12 10	30	22,300	14,700 9,300	12	1900	Failed in tension during soaking Failed in tension during soaking
		22,600		12	1900	
				4	2300	
				4	2300	
					2300	



TABLE IV - MODULUS-OF-RUPTURE STRENGTHS FOR TITANIUM CARBIDE - COBALT CERAMALS

Specimen	Metal (percent by weight)	Density (grams/ml)	Soak		Modulus of rupture (lb/sq. in.)		
			Time (hr)	Temperature (°F)	1600° F	2000° F	2400° F
3B							
5	5	5.06	14	1700	44,300		
6		5.06	15	1700	56,800		
8		5.06	17	2100		40,400	
9		5.08	15	2100		26,100	
15		5.13	4	2100		44,100	
7		5.06	$\frac{1}{6}$	2400			2600
10		5.09	$\frac{1}{6}$	2400			2900
3C							
8	10	----	$16\frac{1}{4}$	1800	50,800		
6		5.22	$16\frac{1}{3}$	1700	73,400		
9		5.19	$14\frac{1}{3}$	2000		39,900	
5		5.18	$15\frac{1}{2}$	2100		39,500	
7		5.19	$\frac{1}{6}$	2400			1700
10		5.18	$\frac{1}{6}$	2400			2000
3D							
6	20	5.35	14	1600	95,200		
11		5.39	$14\frac{1}{2}$	1600	100,800		
39		5.34	4	1700	57,800		
10		5.38	$15\frac{1}{2}$	2100		71,900	
9		5.34	$15\frac{3}{4}$	2100		37,400	
32		5.41	4	2100		29,400	
31		5.46	4	2100		31,700	
7		5.39	$\frac{1}{6}$	2400			2000
8		5.35	$\frac{1}{6}$	2400			2400
3E							
2	30	5.55	$15\frac{1}{2}$	1700	99,300		
5		5.58	$14\frac{3}{4}$	1700	93,400		
1		5.58	13	2100		35,900	
4		5.53	$17\frac{1}{2}$	2100		65,400	
17		5.59	4	2100		22,800	
16		5.54	4	2100		29,600	
3		5.52	$\frac{1}{6}$	2400			2400
6		5.47	$\frac{1}{6}$	2400			2100



TABLE V - MODULUS-OF-RUPTURE STRENGTHS FOR TITANIUM CARBIDE - TUNGSTEN CERAMALS

Specimen	Metal (percent by weight)	Density (grams/ml)	Soak		Modulus of rupture (lb/sq in.)		
			Time (hr)	Temperature (°F)	1600° F	2000° F	2400° F
3F	5	5.21	16 $\frac{1}{4}$	1600	56,700		
1			16 $\frac{1}{4}$	1600	18,100		
2			4	1700	62,900		
8			4	2100		36,600	
7			4	2100		37,700	
4			1 $\frac{1}{6}$	2400			7700
5			1 $\frac{1}{6}$	2400			9100
6	10	5.05	16 $\frac{1}{6}$	1600	43,300		
1			16 $\frac{1}{2}$	1700	51,600		
3			12 $\frac{1}{3}$	2100		14,800	
2			15 $\frac{1}{3}$	2100		16,000	
6			4	2100		23,600	
8			4	2100		32,800	
7			1 $\frac{1}{6}$	2400			19,000
4			1 $\frac{1}{6}$	2400			3,900
5							
3H	20	5.37	15 $\frac{2}{3}$	1600	22,300		
1			17 $\frac{1}{4}$	1700	33,700		
2			12 $\frac{2}{3}$	2100		11,900	
3			16	2100		22,900	
4			4	2100		17,300	
7			1 $\frac{1}{6}$	2400			11,000
6			1 $\frac{1}{6}$	2400			8,100
5							
3I	30	5.88	15 $\frac{1}{2}$	1700	21,500		
1			17 $\frac{3}{4}$	1700	28,000		
3			4	1700	29,700		
7			13 $\frac{1}{4}$	2100		17,000	
2			15	2100		18,500	
4			1 $\frac{1}{6}$	2400			9700
6			1 $\frac{1}{6}$	2400			4800
5							

TABLE VI - MODULUS-OF-RUPTURE STRENGTHS FOR TITANIUM CARBIDE - MOLYBDENUM CERAMALS

Specimen	Metal (percent by weight)	Density (grams/ml)	Soak		Modulus of rupture (lb/sq in.)		
			Time (hr)	Temper- ature (°F)	1600° F	2000° F	2400° F
3J	5	5.06	5	1600	44,100		
3			16	1600	42,100		
2			14 $\frac{1}{2}$	2100		38,300	
1			14 $\frac{1}{3}$	2100		25,300	
4			4	2100		41,400	
7			$\frac{1}{6}$	2400			10,500
5			$\frac{1}{6}$	2400			10,500
6							
3K	10	4.97	16	1700	35,300		
1			16 $\frac{1}{3}$	1700	40,500		
2			4	1700	53,000		
8			14 $\frac{1}{2}$	2100		21,300	
4			12 $\frac{1}{3}$	2100		15,400	
3			4	2100		42,000	
7			$\frac{1}{6}$	2400			20,900
6			$\frac{1}{6}$	2400			16,100
5							
3L	20	5.27	16	1600	25,500		
1			14	1700	33,900		
5			15 $\frac{1}{4}$	2100		29,800	
2			12 $\frac{1}{2}$	2100		30,100	
3			4	2100		24,100	
7			$\frac{1}{6}$	2400			11,700
6			$\frac{1}{6}$	2400			17,200
4							
3M	30	5.74	16	1700	51,200		
2			16	1700	51,000		
1			14 $\frac{1}{2}$	2100		38,400	
3			14 $\frac{1}{3}$	2100		46,500	
4			$\frac{1}{6}$	2400			3100
5			$\frac{1}{6}$	2400			2900
7			$\frac{1}{6}$	2400			4400
8							

TABLE VII - COMPARISON OF STRENGTH-TO-WEIGHT RATIOS
OF TITANIUM CARBIDE PLUS METAL CERAMALS AND
A HIGH-TEMPERATURE ALLOY

Material	Average measured density (grams/ml)	Tensile strength at 1800° F (lb/sq in.)	Strength- to-weight ratio at 1800° F
80-percent titanium carbide (TiC) + 20-percent cobalt (Co)	5.38	34,600	6400
95-percent titanium carbide (TiC) + 5-percent tungsten (W)	5.19	^a 25,000	4800
90-percent titanium carbide (TiC) + 10-percent molybdenum (Mo)	5.10	^a 23,800	4700
High-temperature alloy	8.3	33,000	4000

^aValues calculated from elevated-temperature transverse-bending strength.



TABLE VIII - CHEMICAL ANALYSIS OF TITANIUM CARBIDE PLUS METAL CERAMALS

Specimen	Metal (nominal percent by weight)	Analysis (percent by weight)						
		Titanium	Addition metal			Tungsten (a)	Free carbon	Total carbon
			Cobalt	Tungsten	Molybdenum			
b3B1	5	73.18	4.44			1.28	0.48	17.23
b3B7		73.43	4.48			.60	.67	16.27
b3C5	10	71.30	8.92			2.10	0.42	16.00
b3D1	20	62.83	19.04			0.24	0.34	14.93
c3D1		60.77	18.41			.08	.40	15.06
b3D7		64.83	15.94			.47	.35	14.27
b3E1	30	54.62	28.70			0.10	0.43	12.66
b3E7		54.36	28.74			.10	.37	12.35
b3F3	5	67.50		d10.15			0.05	15.56
b3F5		71.57		10.14			.01	17.52
b3F6		71.99		9.33			.01	17.36
b3G2	10	68.07		15.65			Trace	15.68
b3G4		64.56		15.69			0.04	16.24
b3G6		67.71		15.16			.02	16.41
b3H3	20	58.48		21.95			0.04	14.40
b3H5		61.43		20.02			.01	14.91
b3H6		60.06		24.27			.01	14.96
b3I2	30	52.01		34.08			0.02	13.23
b3I4		52.76		32.98			.02	13.47
e3I4				32.16			.00	12.77
b3I5		50.17		32.14			.04	13.39
c3I6		53.50		33.42			.05	12.84
e3I6				32.97			.00	13.08
b3J1	5	72.38			3.92	6.04	0.01	17.36
b3J4		72.99			4.04	5.56	Trace	17.05
e3K2	10				10.43	5.84	0.00	16.64
b3K3		68.10			8.44	6.60	Trace	16.55
b3K6		67.45			8.72	6.62	.01	16.73
b3L2	20	57.76			17.24	9.36	0.01	15.23
e3L2					18.13	5.12	.00	15.40
b3L3		66.03			16.81	1.59	.00	15.20
b3M3	30	57.61			24.54	3.82	0.00	13.41
b3M4		54.97			26.32	4.56	Trace	13.47
c3M6		48.75			27.87	6.75	.07	13.50
e3M6					28.96	7.17	.00	13.62

^aResults from contamination during milling.

^bAnalysis by commercial laboratory A.

^cAnalysis by commercial laboratory B.

^dIncludes added tungsten and tungsten carbide contamination during milling.

^eAnalysis by fabricator.


 NACA

TABLE IX - DENSITY OF TITANIUM CARBIDE
PLUS METAL CERAMALS

Specimen	Metal (nominal per- cent by weight)	Calculated density ^a (grams/ml)	Average measured density (grams/ml)
Cobalt			
3B	5	5.10	5.08
3C	10	5.21	5.19
3D	20	5.47	5.38
3E	30	5.75	5.54
Tungsten			
3F	5	5.37	5.19
3G	10	5.58	5.08
3H	20	5.06	5.36
3I	30	6.62	5.88
Molybdenum			
3J	5	5.31	5.17
3K	10	5.45	5.10
3L	20	5.76	5.27
3M	30	6.10	5.74

^aNominal analyses plus average tungsten carbide contamination as reported in the chemical analyses for each type ceramal and mechanical mixture of the ingredients are assumed.



TABLE X - COEFFICIENTS OF LINEAR EXPANSION OF
TITANIUM CARBIDE PLUS METAL CERAMALS

Specimen	Metal (percent by weight)	Measured coefficient of linear expansion from room temperature to 1100° F ((in./in.)/°F)	Calculated coef- ficient of linear expansion from room temperature to 1100° F ((in./in.)/°F)
Cobalt			
3B6	5	4.5×10^{-6}	4.3×10^{-6}
3C8	10	4.7	4.5
3D12	20	4.6	4.9
3E11	30	4.9	5.3
Tungsten			
3F8	5	4.1×10^{-6}	4.1×10^{-6}
3G1	10	4.1	4.1
3H1	20	4.0	4.0
3I3	30	4.0	3.9
Molybdenum			
3J2	5	4.1×10^{-6}	4.1×10^{-6}
3K1	10	4.1	4.1
3L5	20	3.9	4.0
3M2	30	3.9	3.9



Page intentionally left blank

Page intentionally left blank

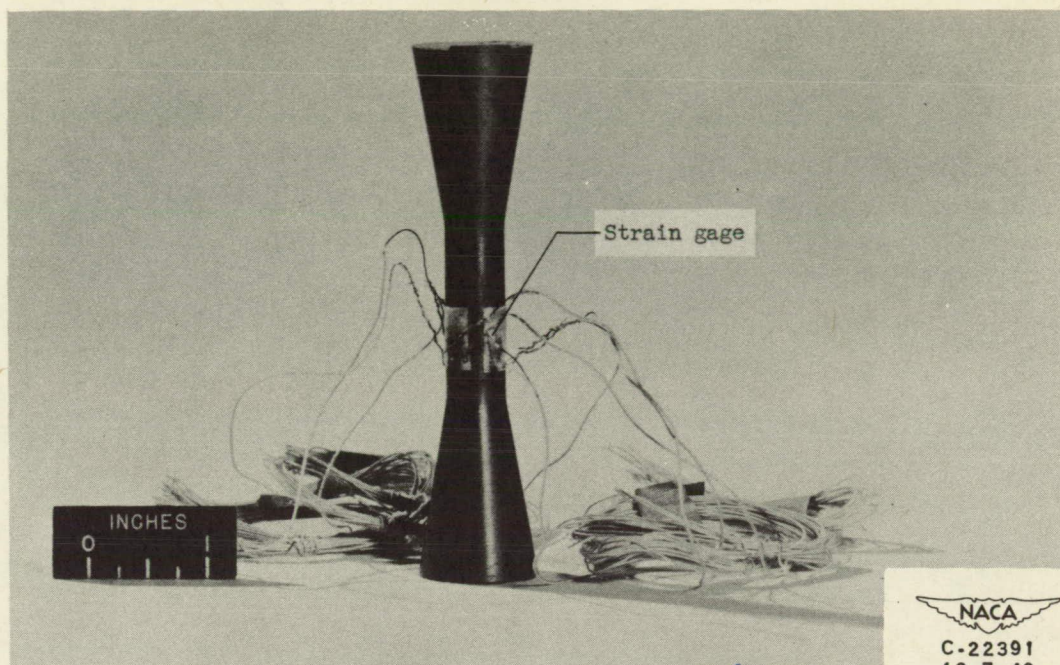


Figure 1. - Tensile-evaluation specimen for brittle materials.

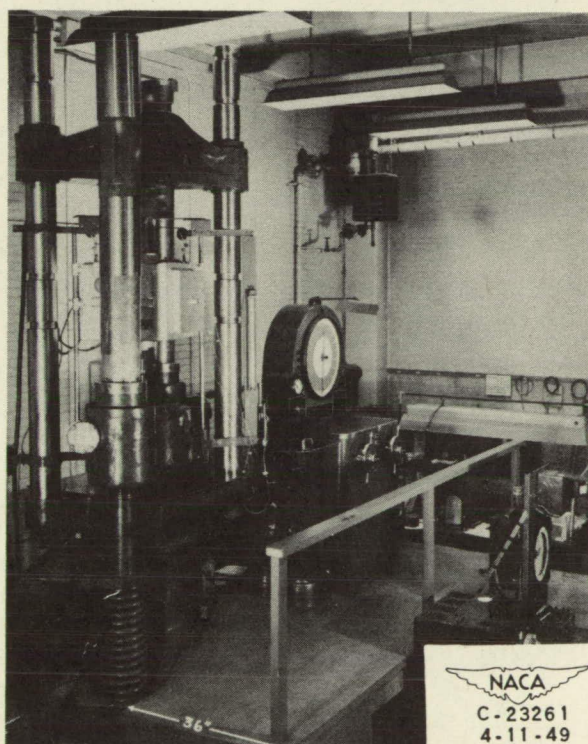


Figure 2. - Tensile-strength evaluation unit.

Page intentionally left blank

Page intentionally left blank

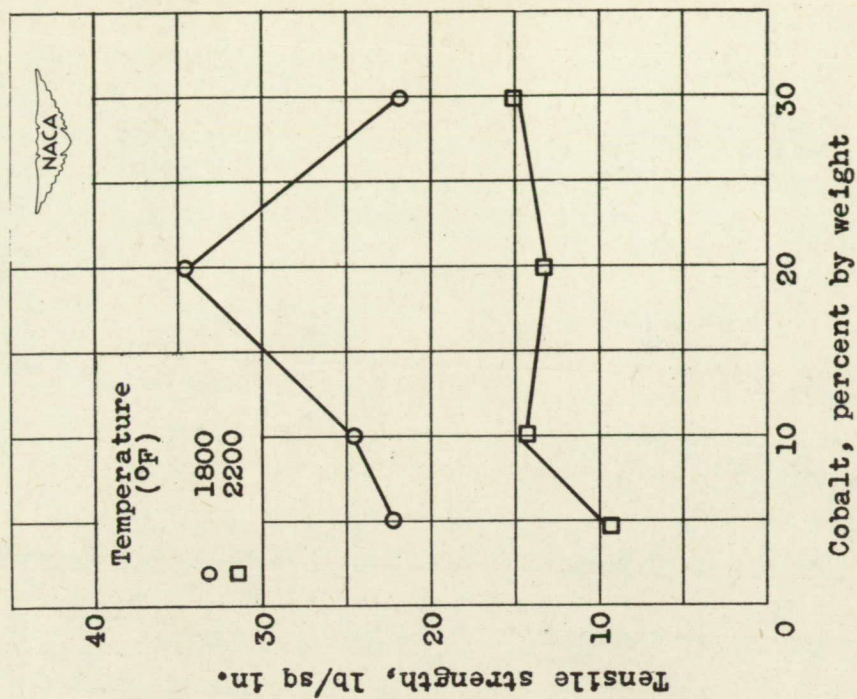


Figure 4. - Tensile strength of titanium carbide - cobalt ceramals at 1800° and 2200° F.

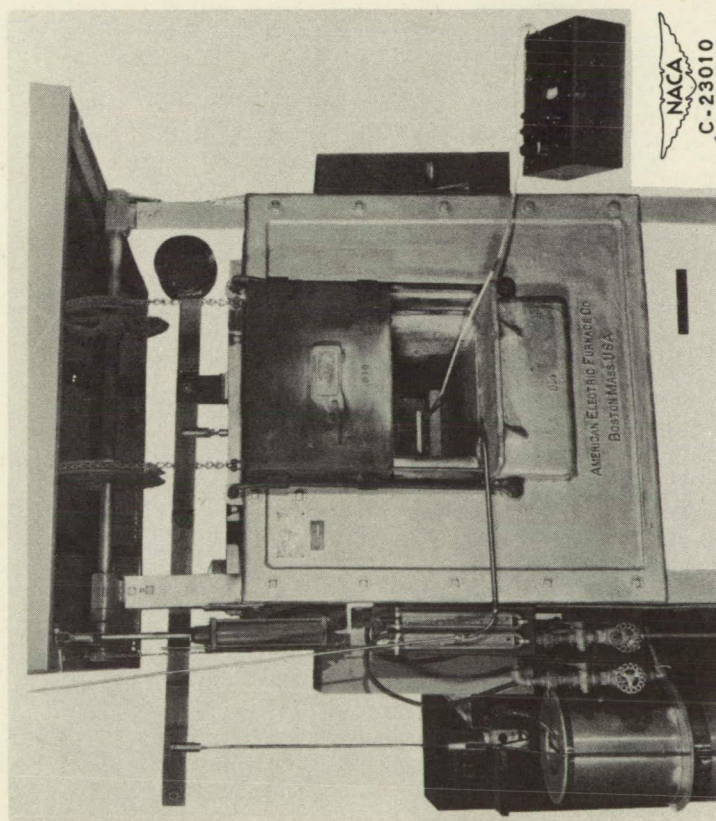


Figure 3. - Modulus-of-rupture evaluation apparatus.

NACA
C-23010
2-24-49

Page intentionally left blank

Page intentionally left blank

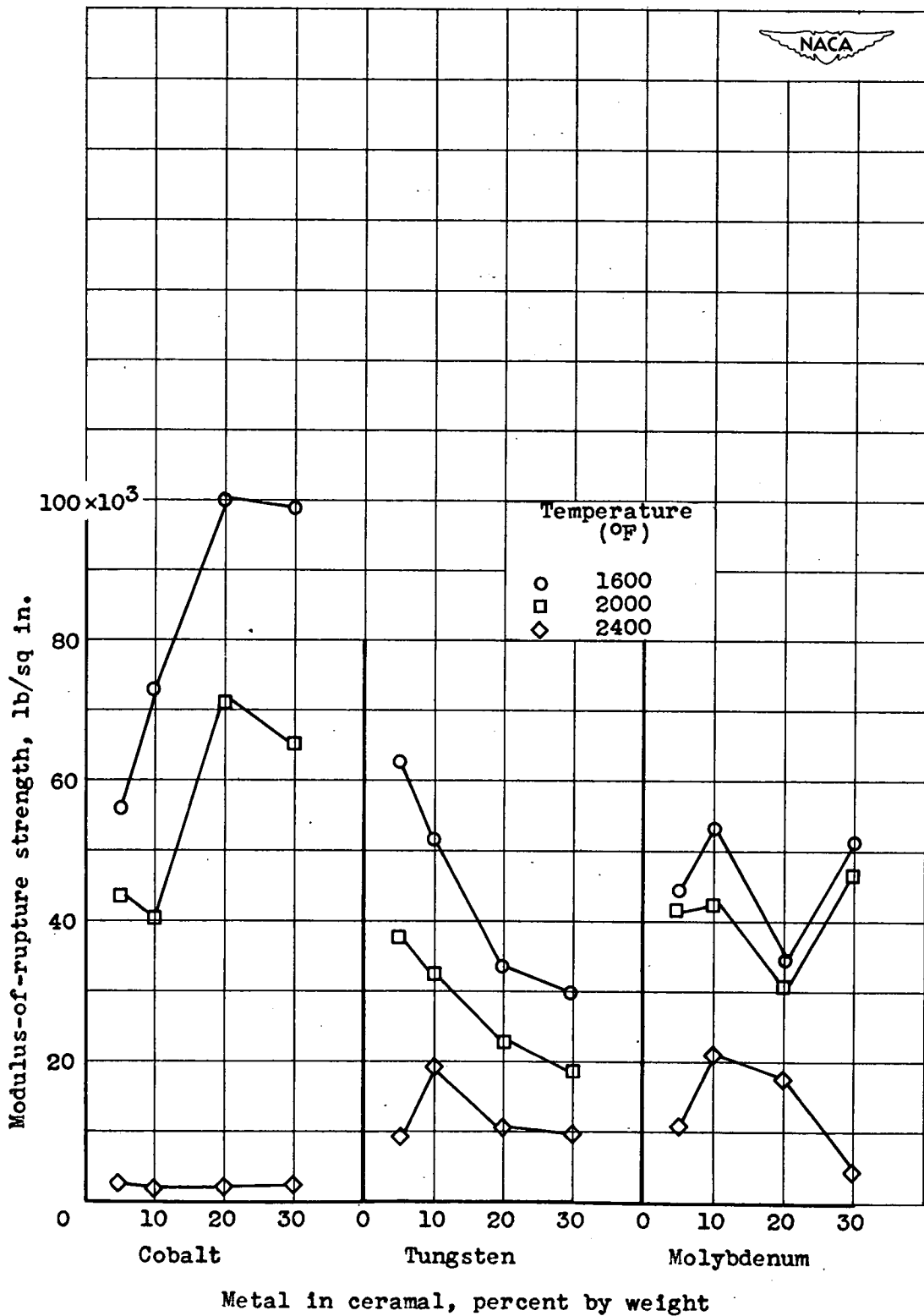


Figure 5. - Trends in modulus-of-rupture strength of titanium carbide ceramals at 1600°, 2000°, and 2400° F.

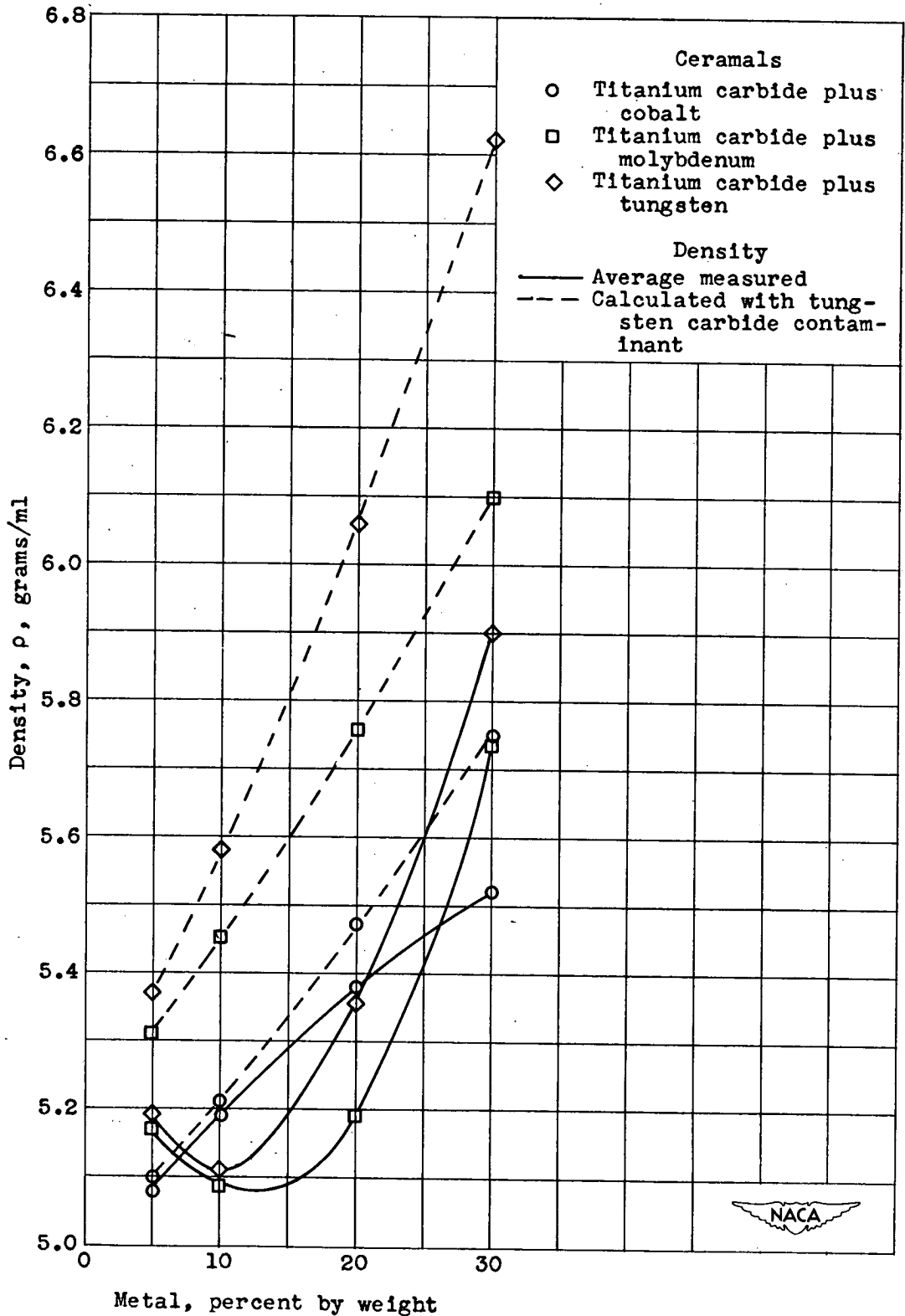
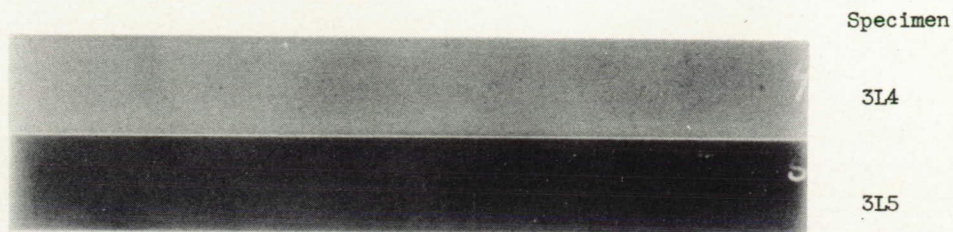


Figure 6. - Average measured and calculated densities of titanium carbide ceramals.



(a) Differences in apparent density.

NACA
C-23262
4-11-49



(b) Chemical segregation.

NACA
C-23263
4-11-49

Figure 7. - Radiographs of modulus-of-rupture specimens showing typical defects as reported in table II.

Page intentionally left blank

Page intentionally left blank

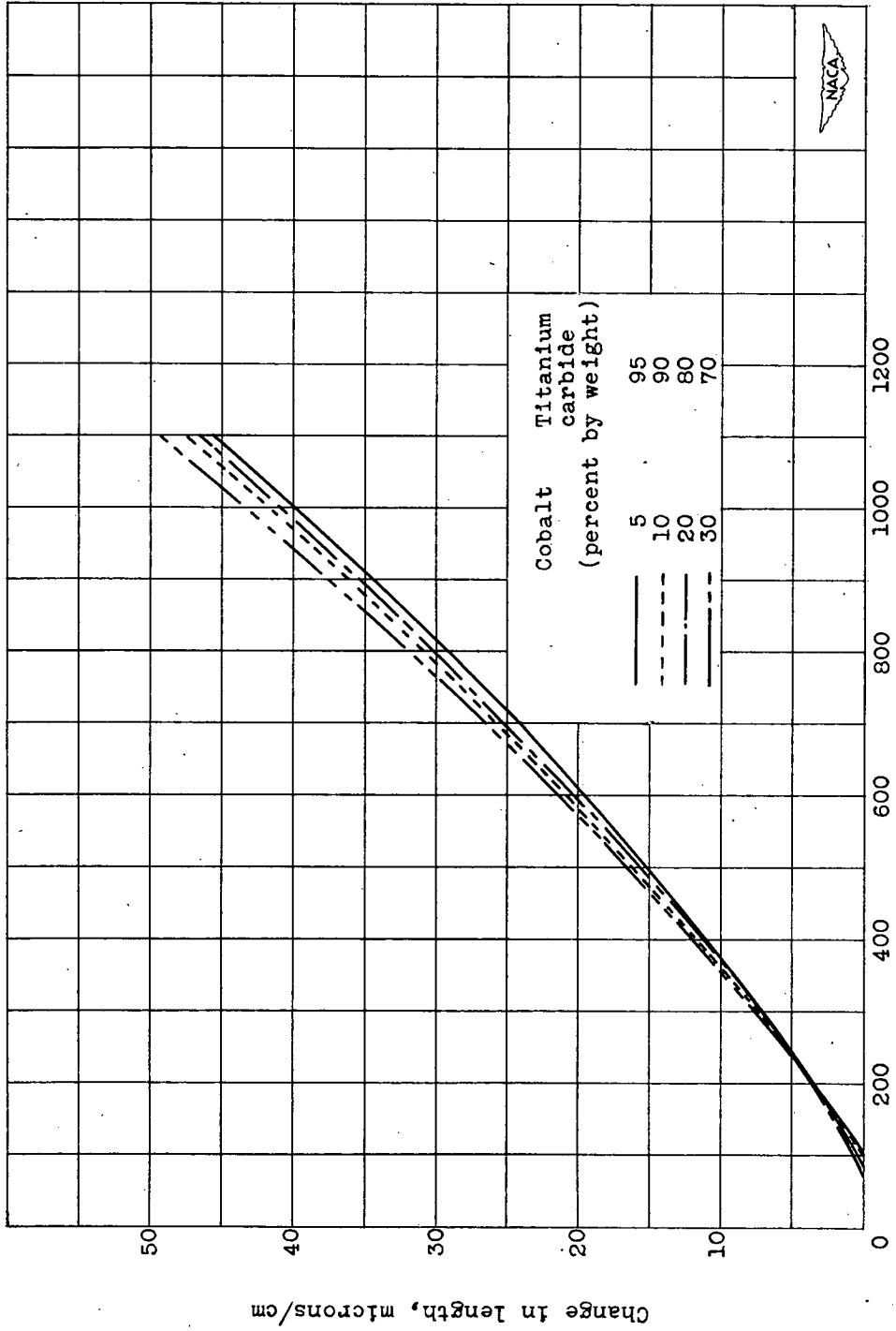
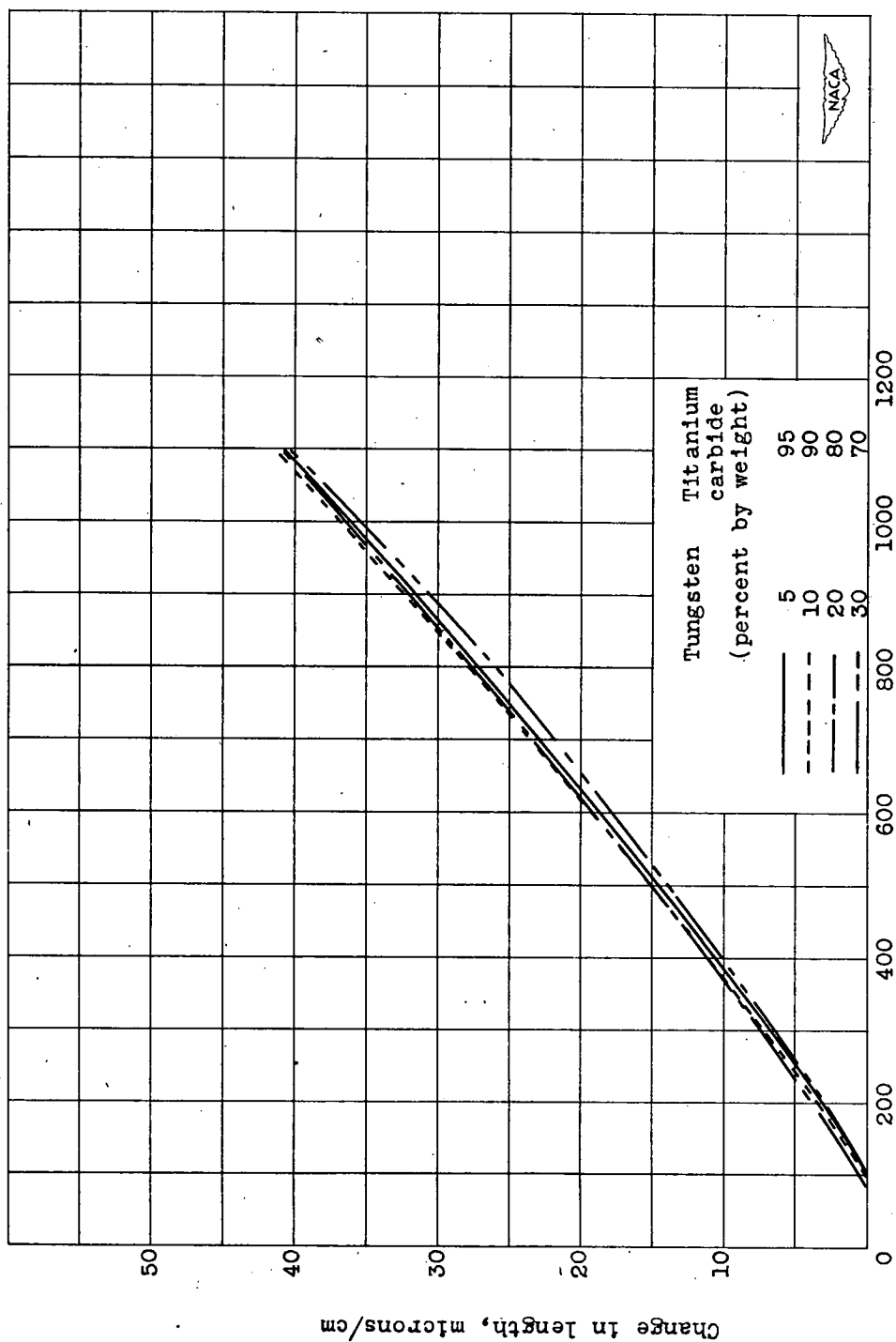


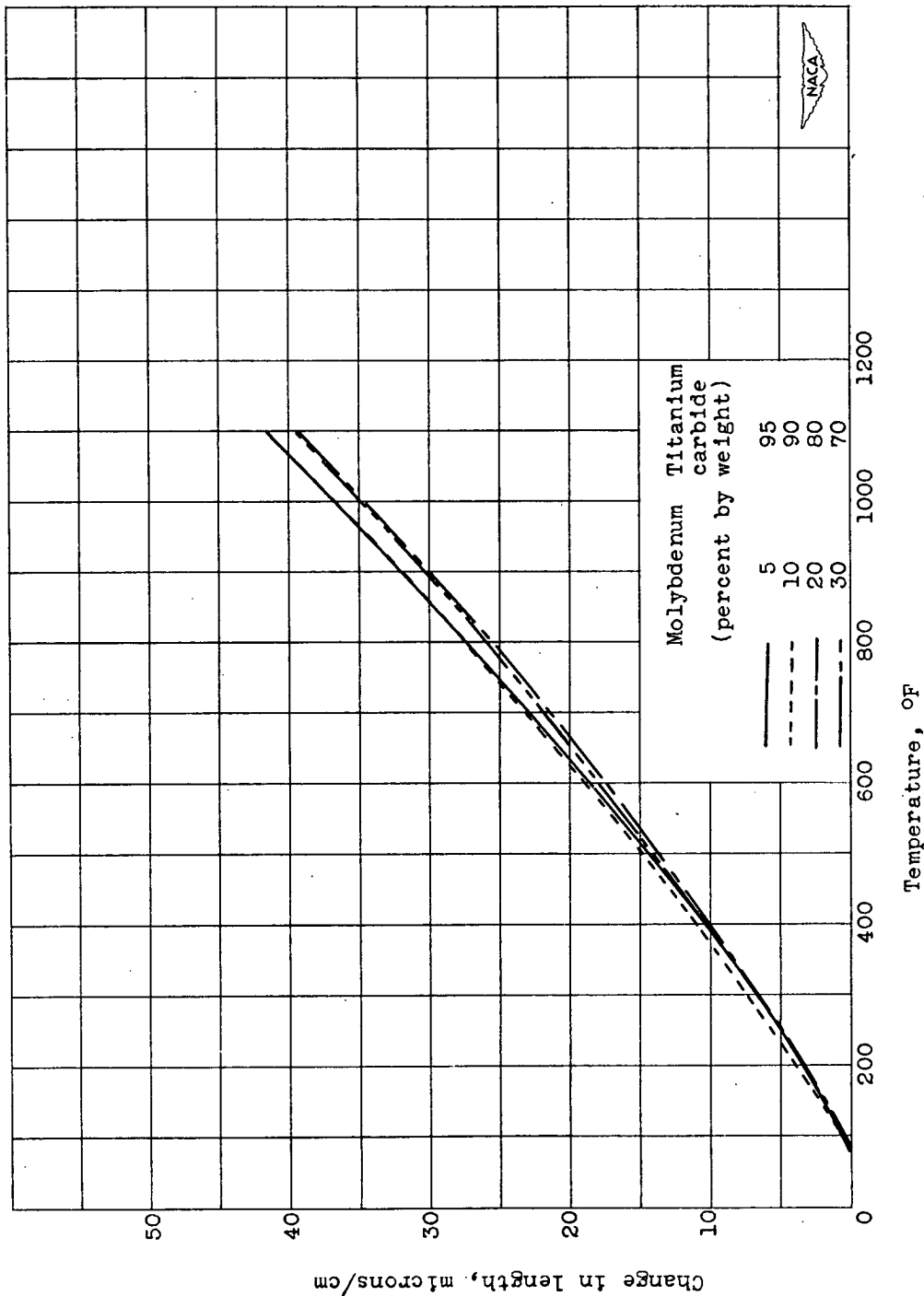
Figure 8. - Coefficients of linear expansion of titanium carbide ceramals.

(a) Titanium carbide plus cobalt.



(b) Titanium carbide plus tungsten.

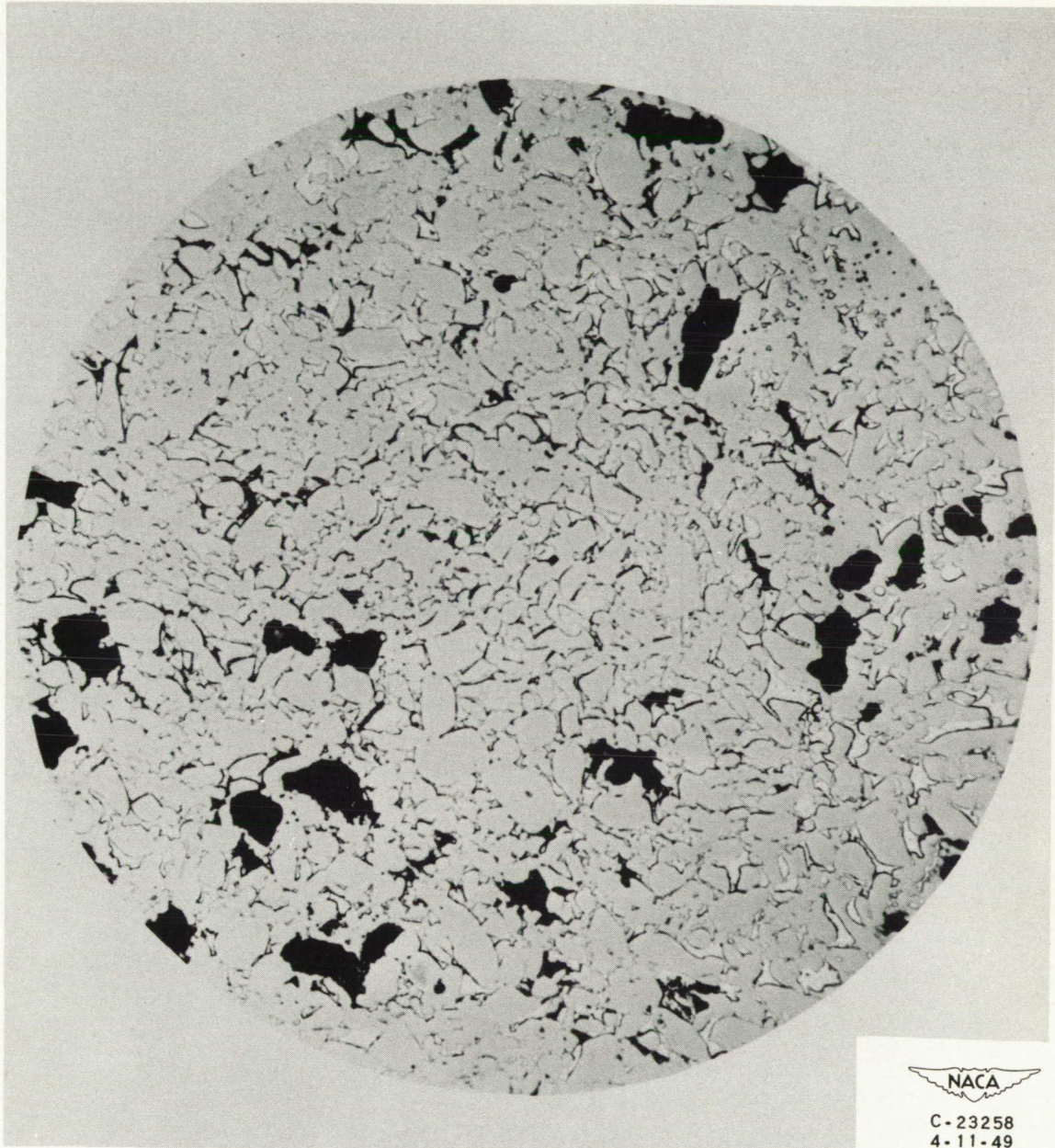
Figure 8. - Continued. Coefficients of linear expansion of titanium carbide ceramals.



(c) Titanium carbide plus molybdenum.
Figure 8. - Concluded. Coefficients of linear expansion of titanium carbide ceramals.

Page intentionally left blank

Page intentionally left blank



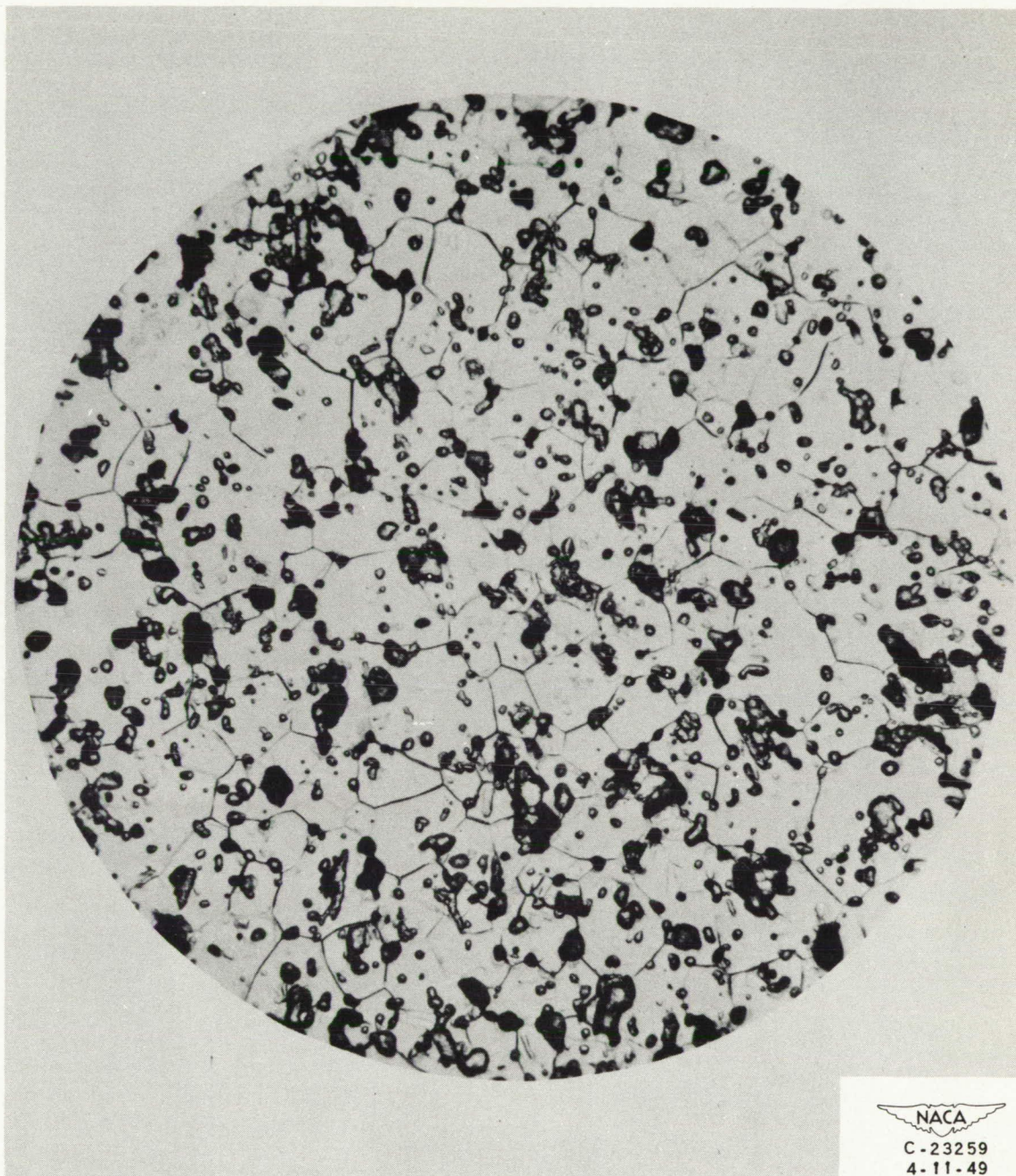
NACA

C-23258
4-11-49

Figure 9. - Ceramal of 70-percent titanium carbide and 30-percent cobalt by weight.
Etched with phosphoric acid H_3PO_4 ; magnification, $\times 750$.

Page intentionally left blank

Page intentionally left blank

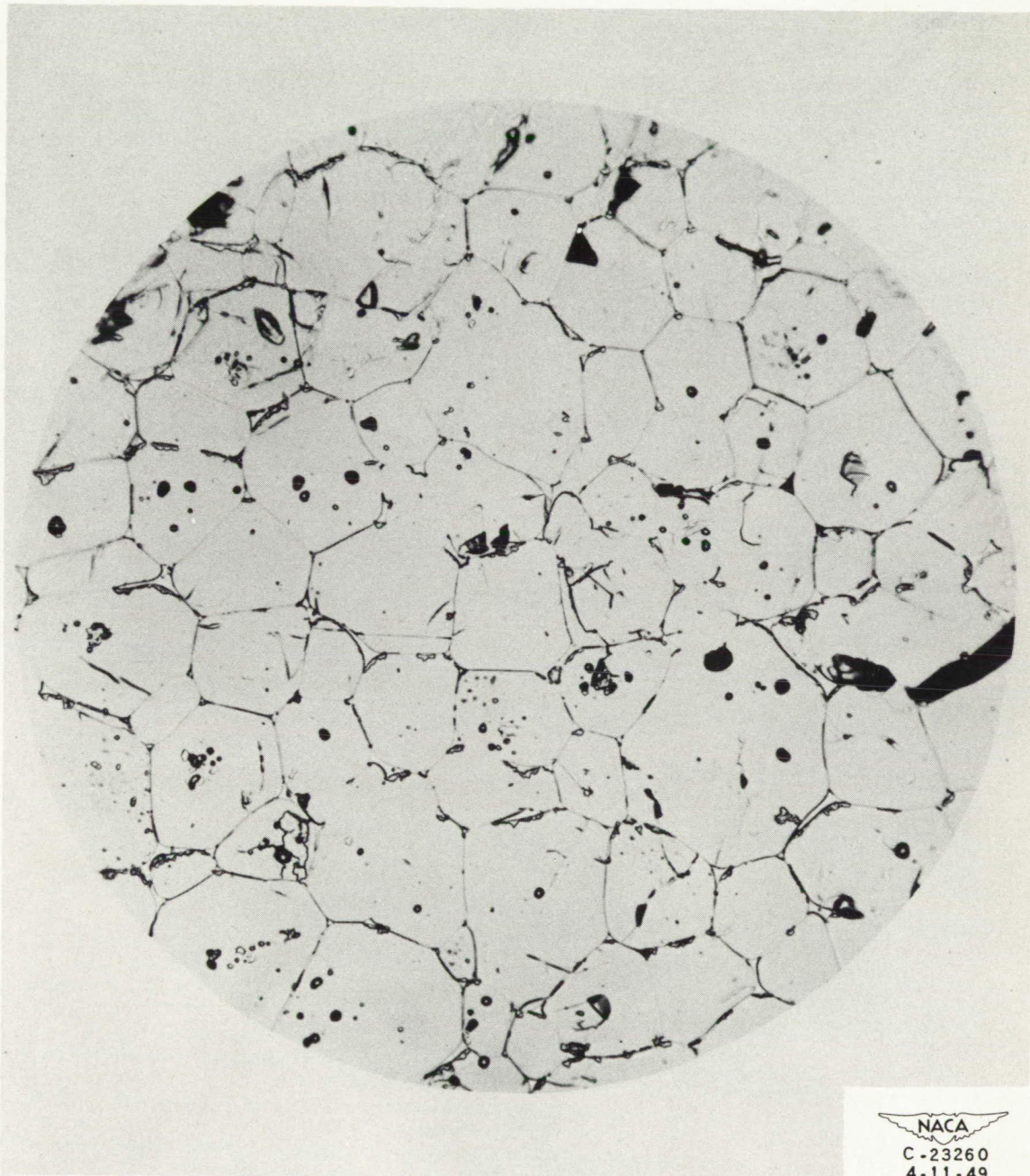


NACA
C-23259
4-11-49

Figure 10. - Ceramal of 70-percent titanium carbide and 30-percent tungsten by weight. Etched with potassium hydroxide plus potassium ferricyanide $\text{KOH} + \text{K}_3\text{Fe}(\text{CN})_6$; magnification, $\times 750$.

Page intentionally left blank

Page intentionally left blank



NACA
C-23260
4-11-49

Figure 11. - Ceramal of 70-percent titanium carbide and 30-percent molybdenum by weight. Etched with potassium hydroxide plus potassium ferricyanide $\text{KOH} + \text{K}_3\text{Fe}(\text{CN})_6$; magnification, $\times 750$.